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SUBLIMATION GROWTH OF LARGE SINGLE CRYSTALS OF BETA
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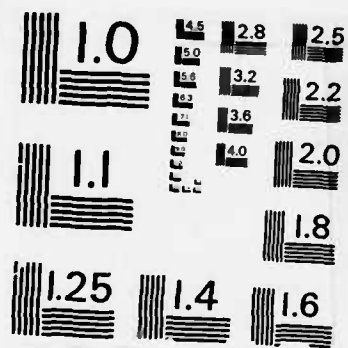
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Technical Progress Report on

"Sublimation Growth of Large Single Crystals of Beta Silicon Carbide"

Contract Number:
N00014-88-C-0596

For Period:
August 15 - December 15, 1988

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Submitted to:

Scientific Officer
Office of Naval Research
Attn: Max N. Yoder, Code 1114SS
Ref: Contract N00014-88-C-0596
800 North Quincy Street
Arlington, Virginia 22217-5000

Source of Funding:

OSD/SDIO/IST

Submitted by:

Dr. Calvin H. Carter, Jr.
Cree Research, Inc.
2810 Meridian Parkway, Suite 176
Durham, NC 27713

January 15, 1989

Distribution authorized to DoD components only, CT; Other requesters must be referred to: Office of Naval Research, ATTN: Code 1114SS, 800 N. Quincy Street, Arlington, VA 22217-5000
Per Mr. Max N. Yoder, ONR/Code 1114SS

22 Feb 89

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Unclassified

SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION Unclassified			1b. RESTRICTIVE MARKINGS None	
2a. SECURITY CLASSIFICATION AUTHORITY Office of Naval Research			3. DISTRIBUTION / AVAILABILITY OF REPORT Approved for public release: Distribution Unlimited	
2b. DECLASSIFICATION / DOWNGRADING SCHEDULE N/A				
4. PERFORMING ORGANIZATION REPORT NUMBER(S) TR 880002-1			5. MONITORING ORGANIZATION REPORT NUMBER(S)	
6a. NAME OF PERFORMING ORGANIZATION Cree Research, Inc.		6b. OFFICE SYMBOL (If applicable)		7a. NAME OF MONITORING ORGANIZATION Office of Naval Research
6c. ADDRESS (City, State, and ZIP Code) 2810 Meridian Parkway, Suite 176 Durham, NC 27713			7b. ADDRESS (City, State, and ZIP Code) 800 North Quincy Street Arlington, VA 22217-5000	
8a. NAME OF FUNDING / SPONSORING ORGANIZATION OSD/SDIO/IST		8b. OFFICE SYMBOL (If applicable)		9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N00014-88-C-0596
8c. ADDRESS (City, State, and ZIP Code) Pentagon Washington, DC 20301-7100			10. SOURCE OF FUNDING NUMBERS	
			PROGRAM ELEMENT NO. 63220C	PROJECT NO. S405012SRR
			TASK NO. 01	WORK UNIT ACCESSION NO.
11. TITLE (Include Security Classification) Sublimation Growth of Large Single Crystals of Beta Silicon Carbide				
12. PERSONAL AUTHOR(S) Calvin H. Carter, Jr.				
13a. TYPE OF REPORT Progress		13b. TIME COVERED FROM 8/15/88 TO 12/15/88		15. PAGE COUNT 12
14. DATE OF REPORT (Year, Month, Day) 1989, January 15				
16. SUPPLEMENTARY NOTATION				
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)	
FIELD	GROUP	SUB-GROUP	semiconductor, silicon carbide, crystal growth, microwave devices	
19. ABSTRACT (Continue on reverse if necessary and identify by block number)				
<p>Beta silicon carbide (β-SiC) possesses a unique combination of properties important for application in high frequency electronic devices capable of operating at high power. The combination of its wide bandgap (2.2 eV @ 27°C), high saturated electron drift velocity (2.5×10^7 cm/sec), high breakdown electric field (4×10^6 V/cm), low dielectric constant (9.7) and high thermal conductivity (5 W / C @ 27°C) give it a figure of merit for high power microwave applications that is 1100 times better than that of Si and 183 times better than that of GaAs. Recent research on SiC has resulted in the fabrication of a variety of electronic devices from both α- and β-SiC. The recent production of large 6H-SiC crystals and their use as substrates for subsequent CVD deposition has resulted in a dramatic decrease in the defect density in CVD grown 6H-SiC films and an increase in device performance. Prior to this contract, there were no β-SiC crystals larger than 2 mm in diameter.</p> <p>Very good results have been achieved during this first reporting period and the primary objective of this Phase I contract has been met. A 9 mm diameter x 1.5 mm thick single crystal of β-SiC was grown and verified by Laue X-ray diffraction. Several thinner single crystals of β-SiC have also been produced.</p>				
20. DISTRIBUTION / AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS			21. ABSTRACT SECURITY CLASSIFICATION Unclassified	
22a. NAME OF RESPONSIBLE INDIVIDUAL Max N. Yoder			22b. TELEPHONE (Include Area Code) (202) 696-4618	22c. OFFICE SYMBOL ONR-1114

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I. Summary

Very good results have been achieved during this first reporting period and the primary objective of this Phase I contract has been met. A 9 mm diameter x 1.5 mm thick single crystal of ^{Beta} β -SiC was grown and verified by Laue X-ray diffraction. Several thinner single crystals of ^{Beta} β -SiC have also been produced.

The crystal growth experiments were conducted in existing crystal growth furnaces designed by Cree personnel for growth of 6H-SiC single crystals. No equipment modifications were required for the growth of β -SiC, only the growth conditions were significantly changed. Future growth experiments will concentrate on improving the quality and size of the β -SiC single crystals.

II. Background

Beta silicon carbide (β -SiC) possesses a unique combination of properties important for application in high frequency electronic devices capable of operating at high power. The combination of its wide bandgap (2.2 eV @ 27°C), high saturated electron drift velocity (2.5×10^7 cm/sec), high breakdown electric field (4×10^6 V/cm), low dielectric constant (9.7) and high thermal conductivity (5 W/C @ 27°C) give it a figure of merit for high power microwave applications that is 1100 times better than that of Si and 183 times better than that of GaAs. Recent research on SiC has resulted in the fabrication of a variety of electronic devices from both α and β -SiC. The recent production of large 6H-SiC crystals and their use as substrates for subsequent CVD deposition has resulted in a dramatic decrease in the defect density in CVD grown 6H-SiC films and an increase in device performance. Prior to this contract, there were no β -SiC crystals larger than ~ 2 mm in diameter. The research reported herein has the objective of growing large single crystals of β -SiC suitable for use as substrates for CVD growth of β -SiC thin films using a sublimation technique similar to that developed for growing large 6H-SiC single crystals.

Since its accidental synthesis during attempts to produce synthetic diamond, SiC has fascinated crystallographers as the archetypal polytypic material. Silicon carbide is known to form over 170 crystal structures (which are created by varying the stacking sequence of the closest packing plane).

There is only one cubic polytype in SiC and it has become accepted practice to refer to this as β -SiC. All of the other non-cubic (hexagonal and rhombohedral) polytypes are referred to collectively as α -SiC.

Although many theories exist to explain the origin of polytypism, none are widely accepted. In addition, research on polytypism reported over the last 30 years has proven very inconsistent and often contradictory. There are certain aspects about the stability of the β -SiC (the polytype of interest here) which at least show trends, if not total consistency. 1) Beta SiC is the preferentially forming polytype between 1200 and 2000°C, especially by solution growth or by pyrolysis of Si and C containing gases. 2) Beta-SiC appears to be stabilized by the presence of a Si rich atmosphere. (Beta is often reported to be a Si rich polytype.¹ 3) Nitrogen seems to stabilize beta, even at temperatures to 2500°C.²

In designing process parameters to grow β -SiC, there are two somewhat competing criteria. The criteria required to stabilize the beta polytype and those required to produce a high quality single crystal. The most important parameters for polytype control are (1) polytype of the seed, (2) orientation of the seed, (3) growth atmosphere and, (4) growth temperature. The crucial parameters for growing a high quality SiC crystal by sublimation are (1) growth temperature (2) thermal gradient, (3) source material, (4) crucible design and (5) growth pressure and evacuation rate.

Probably the most important factors in determining the polytype of a growing SiC crystal are the polytype and orientation of the seed on which it nucleates. Since different polytypes are made up of various stacking arrangements of the closest packed planes (ie. the (0001) planes in α and the (111) in β), these planes are the least desirable to grow on for polytype control because they do not transmit three dimensional information.

Another major factor for polytype control is the growth atmosphere, both Si and C containing components and the surrounding "ambient". The primary parameters determining the Si and C species in the growth crucible are temperature and temperature gradient as well as source powder size and surface area. In general, Si is the predominant gaseous species evolving from the source powder at temperatures below -2380°C.³ Above this temperature, SiC₂ becomes dominant. Since SiC does not sublime as a single species, the Si/C ratio must be controlled by thermal gradient and source to seed distance. Also, it is reported that the Si/C ratio increases as the source powder grain size decreases.¹ However, this effect is primarily attributed to damage created in

the powder by grinding to smaller grain sizes. It is not clear whether there is a dependence between Si/C ratio and grain size for powders that are not crushed during processing. All of the factors discussed above were taken into consideration in the design of the crystal growth experiments.

III. Seed Acquisition

Since no single crystals of β -SiC suitable for use as seeds existed at the start of this contract, the first task was to produce seeds from the best materials available. Just before the contract began, it was discovered that certain processing conditions in the production of large 6H-SiC single crystals produced yellow areas in the crystals which look like β -SiC. One run was conducted for this contract using a wafer that had ~ 50% yellow area as the seed. The run was successful because a large yellow single crystal was produced. However, subsequent electron diffraction analysis revealed that the material was 15R-SiC instead of 3C-SiC.

The next material used as a seed was polycrystalline SiC produced by chemical vapor deposition. This material has been shown⁴ to be primarily β -SiC and although polycrystalline, it has a strong preferred orientation of the (111) plane perpendicular to the growth direction.

Single crystalline thin film (20-40 μ m thick) β -SiC has been the primary seed material used for this research. These films were grown at Cree by chemical vapor deposition on 25 mm diameter (100) silicon wafers. The details of this process are proprietary, but the process is similar to that developed at North Carolina State University under Office of Naval Research sponsorship and described in Reference 5. Initially films ~ 20 μ m thick were used (growing 40 μ m thick films takes many hours) but the seed sublimed before deposition began more often than not. Each of the 25 mm diameter wafers was cut into four 9 mm x 9 mm squares. The silicon was removed from the squares by etching in HF:HNO₃. The deposition surface on some of the samples was polished to a 0.1 μ m diamond finish prior to etching. Growth experiments were conducted using one of three deposition surfaces: 1) unpolished (100) (a carbon face in this polar material), 2) polished (100) or (3) ($\bar{1}00$) a silicon face which is polished by default since the silicon wafer on which it forms is polished. The latter surface was used most often in the experiments.

IV. Powder Acquisition

The source material for sublimation growth is silicon carbide powder. Approximately 3500gm of -10 +100mesh SiC powder has been used to date. In addition, ~500 gm of -100 mesh fines from production powder runs were used to investigate the effect of grain size on β -SiC growth.

V. Crystal Growth

The sublimation technique used for this research involves placing a β -SiC seed crystal into a sealed graphite crucible. The seed is oriented with the growth face down to minimize defects caused by particles. After loading, the crucible is placed in a graphite furnace capable of attaining the required growth temperature (1975-2245°C) and producing a temperature gradient along the length of the crucible. The temperature gradient acts as the driving force for the transport of material from the powder to the seed. The furnace is first evacuated to a pressure of $\sim 1 \times 10^{-5}$ Torr, heated to $\sim 1000^\circ\text{C}$ to degas the powder and crucible, filled with the desired growth atmosphere to ~ 760 Torr, heated to the growth temperature, slowly evacuated to the growth pressure and maintained for the duration of growth. To terminate the growth, the furnace is back filled to 760 Torr and slowly cooled.

A series of crystal growth experiments have been conducted in which the parameters of seed orientation, seed temperature, thermal gradient, seed to source distance, growth atmosphere, or source material were individually varied. Twenty-three crystal growth runs have been made to date. Seeds of (0001) 15R-SiC (optically mistaken for β), polycrystalline CVD SiC and single crystalline (100) β -SiC thin films (both C and Si face) have been used. The best results to date have been using the Si face of a (100) β -SiC thin film (This has also been the most often used seed material). Seed temperatures from 1975-2075°C (in 25° increments) have been investigated with source temperatures from 2140°C to 2245°C (yielding temperature differences from 140 to 225°C). Growth atmospheres of 100% Ar, 90% Ar/ 10% N₂ and 100% N₂ have been used. Very pure SiC powder with grain sizes of -100 mesh and +60-10 mesh SiC powder mixed with 10 w/o -50+100 mesh Si powder have been used as source material.

VI. Analysis of Results

After each run, the deposition on the seed was examined using an optical microscope to determine surface morphology. If the seed sublimed and the deposition nucleated on the graphite underneath, the deposition was polycrystalline and primarily showed hexagonal facets. If epitaxial growth occurred (which is of course, the desired case), the deposition showed the characteristic 90° growth facets of the (100) plane. The thickness and diameter of the crystal were measured and the relative roughness of the growth surface was also evaluated.

The Laue X-ray diffraction method was used to determine whether or not the grown crystal was (100) β -SiC. The patterns were compared against one taken from a 40 μm thick single crystal thin film of β -SiC grown on Si by CVD (Figure 1). Since this film is relatively thin for X-ray diffraction, some of the spots are quite weak.

As mentioned earlier, the first growth run conducted for this contract used a SiC wafer with a large portion of a yellow polytype (the remainder was green 6H-SiC) which initially was thought to be β -SiC. The run produced a 20 mm diameter x 5 mm thick single crystal of the yellow polytype which was later determined to be 15R-SiC by electron diffraction. When desired, Cree has been able to grow both 15R and 4H-SiC but all production emphasis has been to grow 6H-SiC which is done >95% of the time.

One run was also conducted using polycrystalline SiC grown by CVD as a seed. This material is primarily β -SiC and has a strong preferred orientation of the (111) plane in the growth plane. This run was made in a Ar atmosphere at a seed temperature of 2000°C and source temperature of 2140°C. The resulting deposition on the seed was polycrystalline (~2 mm thick) and green in color. The grains were primarily hexagonal which is characteristic of (0001) α -SiC. However, the deposition on the graphite surrounding the seed was yellow in color. Some of this deposit was removed and analyzed by powder x-ray diffraction. These tiny crystals (~100 μm) were primarily (>90%) β -SiC.

After this run, seeds of thin films of β -SiC were available. The first films available were ~20 μm thick and often broke during loading or sublimed prior to deposition. Three runs were made using these thin films, the last of which showed epitaxial growth on ~1/2 of its area. However, later Laue X-ray

diffraction analysis showed that this (and all subsequent runs conducted in pure Ar) was single crystalline α -SiC.

During this time a very long (14 hr) CVD growth run was made which produced films $\sim 40\text{ }\mu\text{m}$ thick. They were prepared as seeds as described in previous section and all subsequent runs used these (or films from a later duplicate CVD run) as seeds. Eighteen runs have been made with these seeds to date of which three will be described in detail here. General trends of other run conditions will also be discussed.

As mentioned previously, three seed faces were used for these experiments. The best results were obtained using the Si face of the (100) films. This surface was polished by default because the Si on which it was grown (and removed from) was polished. This face yielded crystals with the best surface morphology.

Seed temperatures from 1975 to 2075°C have been used. The surface morphology was smoother for crystals grown at higher temperatures, but above 2025°C the crystals were usually α -SiC (one run at 2075°C yielded β -SiC). The optimum seed temperature was found to be 2025°C. Source temperatures from 2140 to 2245°C have been used. At low thermal gradients less material is moved and the morphology shows holes in the crystal. The optimum source temperature for a seed temperature of 2025°C appears to be 2225°C. No difference was seen between runs using the two different sizes of source material (-100 mesh and +60 -10 mesh), however the addition of 10% free Si to the SiC powder seems to improve the growth of β -SiC in a nitrogen atmosphere.

By far the greatest factor in the successful growth of β -SiC crystals was the use of a nitrogen atmosphere as opposed to argon. We were not able to grow β -SiC under any of the conditions used in argon. Beta-SiC was grown under all conditions using a pure nitrogen atmosphere at temperatures $\leq 2025^\circ\text{C}$, but the quality of the crystals changed depending on the growth parameters.

Figure 2 shows a photomicrograph of the surface of a crystal grown in Ar at seed and source temperatures of 2075°C and 2235°C, respectively. The surfaces of the crystals are very shiny which makes photographing them very difficult. The source powder was +60 -10 mesh pure SiC, the seed was the Si face of a β -film and the pressure was maintained at 760 Torr for the duration of the run (16 hrs.)

The resulting crystal was 9 mm in diameter and 0.4 mm thick. The crystal was light yellow/green in color. As seen in Figure 2, the surface

morphology showed the characteristic cross-hatch (100) features. However, the Laue X-ray pattern, shown in Figure 3, revealed that the deposited crystal was α -SiC.

The run conditions of the crystal shown in Figure 4 were the same as those for Figure 2 except the source material contained 10 w/o free Si and the growth atmosphere was pure nitrogen. The resulting crystal looked very much like the one in Figure 2 except the color was very dark green / black. However, the Laue pattern shown in Figure 5 (a weak image) shows that the crystal is single crystalline β -SiC.

The largest and best crystal grown to date is shown in Figure 6. This crystal is 9 mm in diameter and 1.5 mm thick. It was grown in nitrogen using a seed temperature of 2025°C and a source temperature of 2225°C. The source material contained 10 w/o free Si. The seed was the Si face of a β -SiC thin film and the nitrogen pressure was maintained at 760 Torr throughout the 16 hr. growth period (This crystal is thicker because of the larger thermal gradient). The Laue pattern of this crystal is shown in Figure 7 and shows that it is definitely β -SiC.

VII. Plans for Remainder of Contract

Several more crystal growth runs will be conducted concentrating on growing thicker crystals and improving crystal quality. Growth runs will be conducted in N_2 at higher temperatures with larger ($>200^\circ\text{C}$) thermal gradients. Runs may be made with more than 10% Si powder mixed with the SiC powder but this is very hazardous to the furnace hot zone. Also, the crystals will be sectioned so that transmission optical microscopy can be used to better judge their crystalline quality during the next reporting period.

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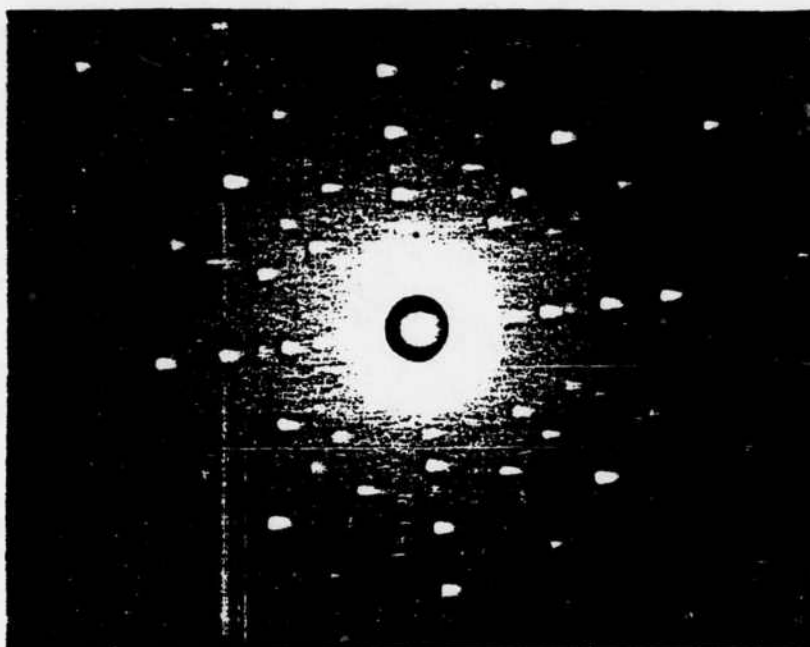


Figure 1. Laue X-ray pattern of 40 μm thick single crystal $\beta\text{-SiC}$ film grown by CVD on (100) Si. (Si removed)



Figure 2. Optical photomicrograph of crystal surface grown at 2075°C in argon (7X).

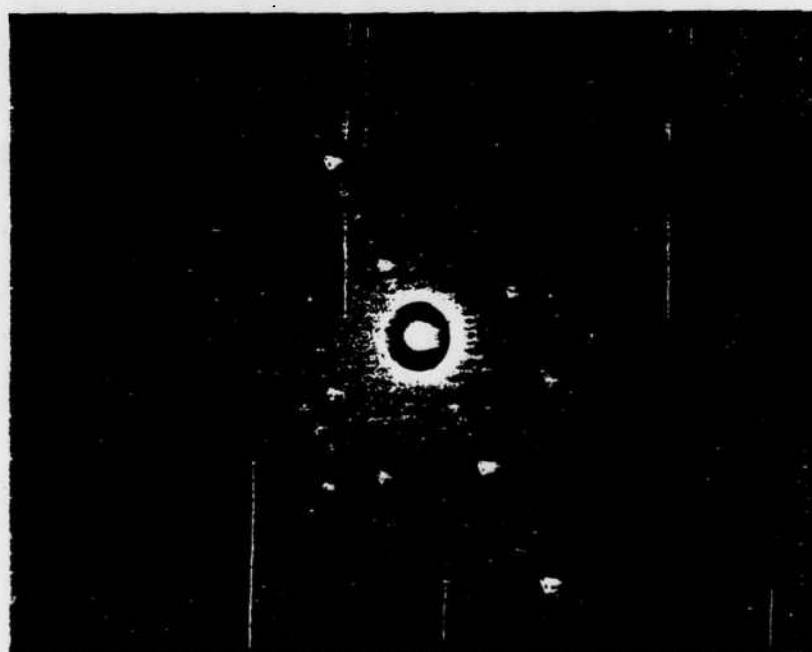


Figure 3. Laue X-ray pattern of crystal shown in Figure 2.

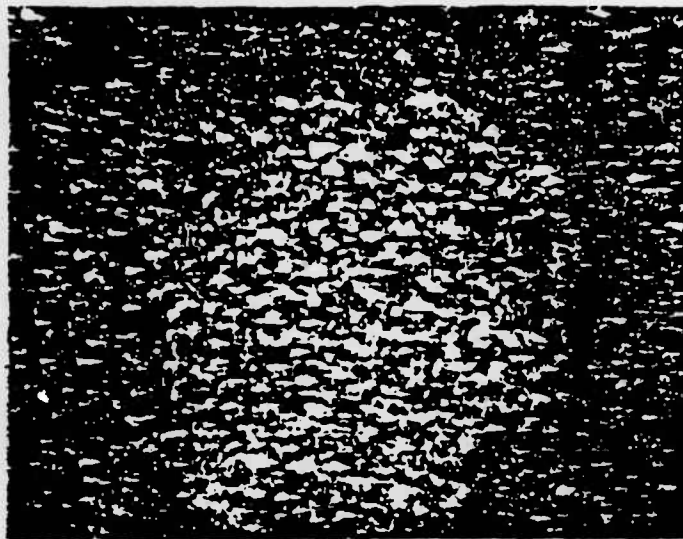


Figure 4. Optical photomicrograph of crystal surface grown at 2075°C in nitrogen (7X).

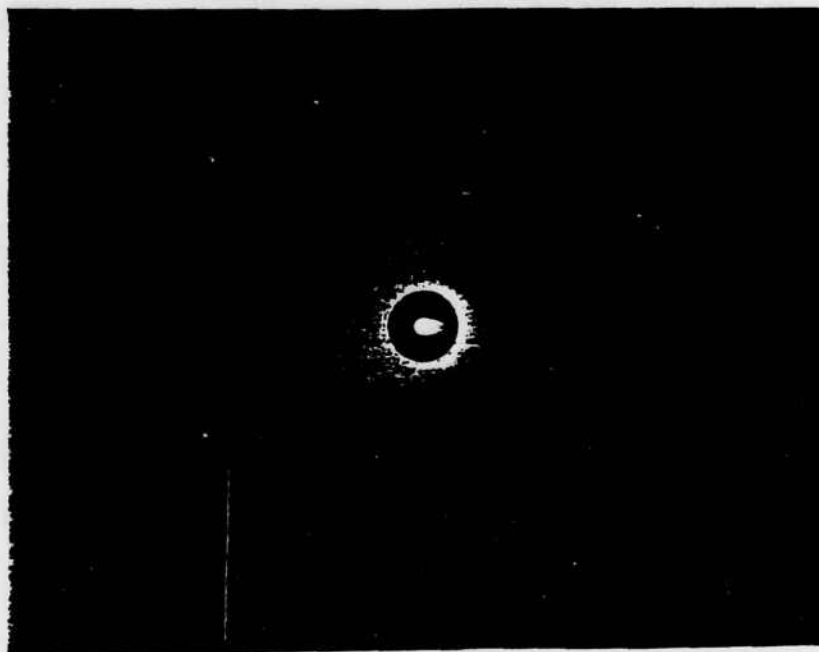


Figure 5. Laue X-ray pattern of crystal shown in Figure 5.

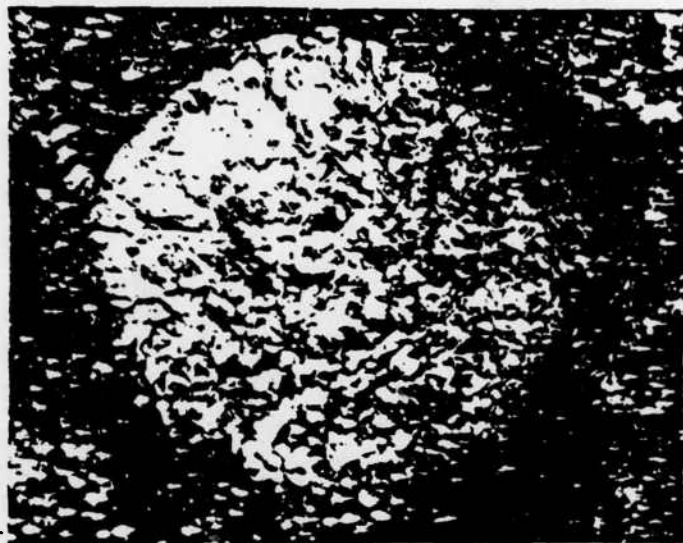


Figure 6. Optical photomicrograph of crystal surface grown at 2025°C in nitrogen (7X).

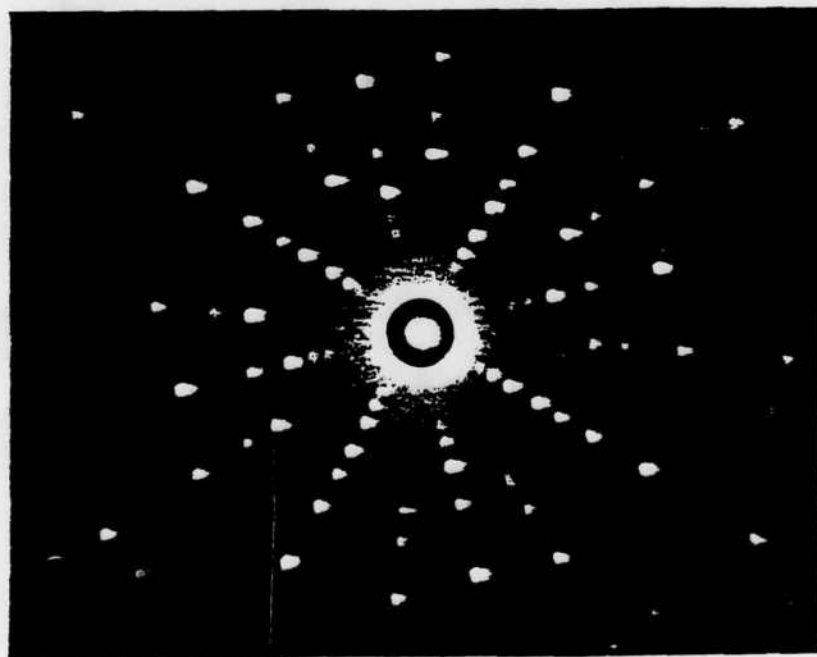


Figure 7. Laue X-ray pattern of crystal shown in Figure 6.

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